

# PATENT ABSTRACTS OF JAPAN

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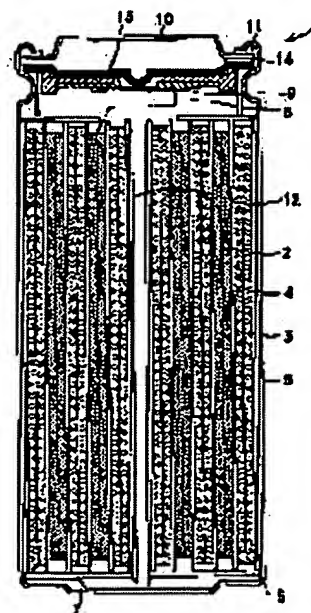
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(54) POSITIVE ACTIVE MATERIAL AND NON-AQUEOUS ELECTROLYTE BATTERY, AND THEIR MANUFACTURING METHOD

(57)Abstract:

PROBLEM TO BE SOLVED: To improve a cycle characteristic at a high temperature.

SOLUTION: A non-aqueous electrolyte battery is comprised of a positive electrode, a negative electrode, and a non-aqueous electrolyte. The positive electrode contains a lithium transition metal composite oxide, which is represented by a general formula  $\text{LiCo}_x\text{AyBzO}_2$ . (in the formula, A represents at least one kind selected from among Al, Cr, V, Mn, or Fe, B represents at least one kind selected from Mg or Ca, and x, y, z are in the following ranges:  $0.9 \leq x < 1$ ;  $0.001 \leq y \leq 0.05$ ; and  $0.001 \leq z \leq 0.05$ ), as a positive active material.



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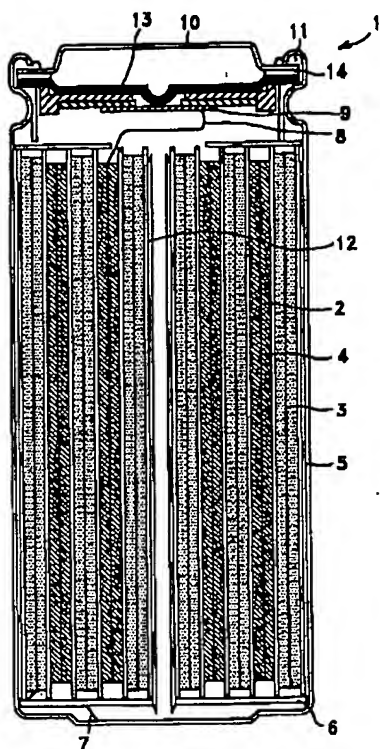
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1. Untranslatable words are replaced with asterisks (\*\*\*\*).
2. Texts in the figures are not translated and shown as it is.

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**CLAIMS**

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**[Claim(s)]**

[Claim 1] General formula  $\text{LiCo}_x\text{A}_y\text{B}_z\text{O}_2$  (A expresses among a formula at least one sort chosen from aluminum, Cr, V, Mn, or Fe, and B expresses at least one sort chosen from Mg or Ca.) Moreover, x, y, and z are the number of the ranges of  $0.9 \leq x < 1$ ,  $0.001 \leq y \leq 0.05$ , and  $0.001 \leq z \leq 0.05$ , respectively. Positive active material characterized by containing the lithium transition metal multiple oxide expressed.

[Claim 2] Have nonaqueous electrolyte which intervenes between a positive electrode, a negative electrode, and a positive electrode and a negative electrode, and [ the above-mentioned positive electrode ] As positive active material, it is a general formula  $\text{LiCo}_x\text{A}_y\text{B}_z\text{O}_2$  (A expresses among a formula at least one sort chosen from aluminum, Cr, V, Mn, or Fe, and B expresses at least one sort chosen from Mg or Ca.). Moreover, x, y, and z are the number of the ranges of  $0.9 \leq x < 1$ ,  $0.001 \leq y \leq 0.05$ , and  $0.001 \leq z \leq 0.05$ , respectively. Nonaqueous electrolyte cell characterized by containing the lithium transition metal multiple oxide expressed.

[Claim 3] The compound of at least one sort of elements chosen from a cobalt compound, a lithium compound, an aluminium and chromium, vanadium, manganese, or iron, By calcinating the mixture obtained by the mixing process which mixes the compound of at least one sort of elements chosen from magnesium or calcium at a predetermined rate, and the above-mentioned mixing process General formula  $\text{LiCo}_x\text{A}_y\text{B}_z\text{O}_2$  (A expresses among a formula at least one sort chosen from aluminum, Cr, V, Mn, or Fe, and B expresses at least one sort chosen from Mg or Ca.) Moreover, x, y, and z are the number of the ranges of  $0.9 \leq x < 1$ ,  $0.001 \leq y \leq 0.05$ , and  $0.001 \leq z \leq 0.05$ , respectively. Have the baking process which obtains the compound expressed and it sets to the above-mentioned mixing process. The manufacture method of the positive active material characterized by using magnesium carbonate or calcium carbonate as a compound of at least one sort of elements chosen from magnesium or calcium.

[Claim 4] When it is the manufacture method of the nonaqueous electrolyte cell equipped with the nonaqueous electrolyte which intervenes between a positive electrode, a negative electrode, and a positive electrode and a negative electrode and the above-mentioned positive electrode is produced, a cobalt compound, The compound of at least one sort of elements chosen from a lithium compound, an aluminium and chromium, vanadium, manganese, or iron, By calcinating the mixture obtained by the mixing process which mixes the compound of at least one sort of elements chosen from magnesium or calcium at a predetermined rate, and the above-mentioned mixing process General formula  $\text{LiCo}_x\text{A}_y\text{B}_z\text{O}_2$  (A expresses among a formula at least one sort chosen from aluminum, Cr, V, Mn, or Fe, and B expresses at least one sort chosen from Mg or Ca.) Moreover, x, y, and z are the number of the ranges of  $0.9 \leq x < 1$ ,  $0.001 \leq y \leq 0.05$ , and  $0.001 \leq z \leq 0.05$ , respectively. Have the baking process which obtains the compound expressed and it sets to the above-mentioned mixing process. The manufacture method of the nonaqueous electrolyte cell characterized by using magnesium carbonate or calcium carbonate as a compound of at least one sort of elements chosen from magnesium or calcium.

## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the positive active material containing a lithium transition metal multiple oxide, the nonaqueous electrolyte cells using the positive active material, and those manufacture methods.

[0002]

[Description of the Prior Art] The demand of high-capacity-izing and a weight saving is becoming strong to the secondary battery as the power supply for a drive with the miniaturization of various electric devices, and cordless-izing in recent years. Since the lithium secondary battery can attain high capacity-ization as compared with the conventional secondary battery, various proposals are made to the cell using dope and dedope of the lithium ion.

[0003] As positive active material of the above-mentioned cell, the lithium transition metal multiple oxide of  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$ ,  $\text{LiMn}_2\text{O}_4$ , and  $\text{LiFePO}_4$  grade is known. Especially,  $\text{LiCoO}_2$  takes a lamellar structure advantageous to diffusion of a lithium ion, and to dedope and re-dope of a lithium ion, since structure is stable, utilization precedes it. Moreover, although  $\text{LiNiO}_2$  takes a lamellar structure similarly and has advantages, such as low cost and high capacity As compared with  $\text{LiCoO}_2$ , the phase change accompanying dedope and re-dope of a lithium ion is intense, when it uses as positive active material of a lithium ion battery, a

lamellar structure collapses in connection with a charge-and-discharge cycle, and there is a fault of causing capacity lowering.

[0004] About  $\text{LiNiO}_2$ , the way a different-species element replaces some nickel has been examined as a method for improving the above-mentioned fault. As it is in JP,H5-325966,A or JP,H5-299092,A, in order [ for example, ] to stabilize a lamellar structure The way Cobalt and manganese replace some nickel, and the way sodium or potassium replaces some lithium in order to maintain the lithium layer to which lithium was dedoped and became unstable at the time of charge, as it is in JP,H6-150929,A again have been proposed.

[0005] Moreover, as how to replace by two or more elements is also examined to nickel, for example, it is in JP,H9-92285,A By replacing by Cobalt, an aluminium, boron, and two or more elements chosen from magnesium The example which has improved the charge-and-discharge cycle characteristic, and the example which has improved a cycle characteristic, a rate characteristic, and the reliability of a cell by replacing by transition metal elements, such as magnesium, boron, or gallium, as it is in JP,H10-208744,A are reported.

[0006]

[Problem to be solved by the invention] However, in  $\text{LiCoO}_2$ , since the lamellar structure is originally stable, the lithium ion battery which uses  $\text{LiCoO}_2$  has a good cycle characteristic as compared with the case where  $\text{LiNiO}_2$  is used. For this reason,  $\text{LiCoO}_2$  did not need to perform different-species element displacement etc., and practical use has been presented with it. However, the resistance to environment for which high temperature-ization of instrument bulk temperature is progressing by the densification of an integrated circuit in recent years and improvement in the speed, and a portable device is asked is also becoming severe. For this reason, to aim at use expansion of a lithium ion battery, the cycle characteristic at the time of high temperature etc. also needs to raise the resistance to environment of a cell.

[0007] [ the different-species element displacement of  $\text{LiCoO}_2$  ] As it is in JP,S62-124707,A, improvement in the electronic conduction nature by replacing Cobalt with an aluminium, indium, and tin and improvement in the cycle characteristic by replacing Cobalt from boron in JP,H4-253162,A, bismuth, and lead are reported.

[0008] However, when this invention persons replaced Cobalt of  $\text{LiCoO}_2$  with an aluminium, indium, and tin, charge-and-discharge efficiency or capacity fell remarkably. Moreover, when boron, bismuth, and lead replaced Cobalt, the preservation characteristics at the time of high temperature fell remarkably. It must be said that it is inadequate practically in any case. Moreover, also in JP,H9-92285,A, when an aluminium or magnesium replaces a part of  $\text{LiCoO}_2$ , there is a description that a cycle characteristic gets worse conversely.

[0009] This invention is proposed in view of the conventional actual condition which was mentioned above, and aims at offering the positive active material which raised the hot cycle

characteristic, the nonaqueous electrolyte cells using it, and those manufacture methods.

[0010]

[Means for solving problem] The positive active material of this invention is a general formula  $\text{LiCo}_x\text{A}_y\text{B}_z\text{O}_2$  (A expresses among a formula at least one sort chosen from aluminum, Cr, V, Mn, or Fe, and B expresses at least one sort chosen from Mg or Ca.). Moreover, x, y, and z are the number of the ranges of  $0.9 \leq x < 1$ ,  $0.001 \leq y \leq 0.05$ , and  $0.001 \leq z \leq 0.05$ , respectively. It is characterized by containing the lithium transition metal multiple oxide expressed.

[0011] [ the positive active material concerning this invention which was mentioned above ]

Since the compound which dissolved combining the 1st group which consists of aluminum, Cr, V, Mn, or Fe, and the 2nd group which consists of Mg or Ca in a specific quantity in a part of Cr in  $\text{LiCoO}_2$  is used, the stability not only at the time of ordinary temperature but the time of high temperature improves.

[0012] Moreover, the nonaqueous electrolyte cell of this invention is equipped with the nonaqueous electrolyte which intervenes between a positive electrode, a negative electrode, and a positive electrode and a negative electrode, and [ the above-mentioned positive electrode ] As positive active material, it is a general formula  $\text{LiCo}_x\text{A}_y\text{B}_z\text{O}_2$  (A expresses among a formula at least one sort chosen from aluminum, Cr, V, Mn, or Fe, and B expresses at least one sort chosen from Mg or Ca.). Moreover, x, y, and z are the number of the ranges of  $0.9 \leq x < 1$ ,  $0.001 \leq y \leq 0.05$ , and  $0.001 \leq z \leq 0.05$ , respectively. It is characterized by containing the lithium transition metal multiple oxide expressed.

[0013] [ the nonaqueous electrolyte cell concerning this invention which was mentioned above ]

Since the positive active material which comes to dissolve in a specific quantity combining the 1st group which consists of aluminum, Cr, V, Mn, or Fe, and the 2nd group which consists of Mg or Ca in a part of Cr in  $\text{LiCoO}_2$  is used, the stability not only at the time of the ordinary temperature of the positive active material concerned but the time of high temperature improves. And the nonaqueous electrolyte cell of this invention using such positive active material becomes the thing excellent in the charge-and-discharge characteristics at the time of high temperature.

[0014] The manufacture method of the positive active material of this invention A cobalt compound and a lithium compound, The compound of at least one sort of elements chosen from an aluminium, chromium, vanadium, manganese, or iron, By calcinating the mixture obtained by the mixing process which mixes the compound of at least one sort of elements chosen from magnesium or calcium at a predetermined rate, and the above-mentioned mixing process General formula  $\text{LiCo}_x\text{A}_y\text{B}_z\text{O}_2$  (A expresses among a formula at least one sort chosen from aluminum, Cr, V, Mn, or Fe, and B expresses at least one sort chosen from Mg or Ca.) Moreover, x, y, and z are the number of the ranges of  $0.9 \leq x < 1$ ,  $0.001 \leq y \leq 0.05$ , and

0.001 $\leq$ z $\leq$ 0.05, respectively. It has the baking process which obtains the compound expressed. And the manufacture method of the positive active material of this invention is characterized by using magnesium carbonate or calcium carbonate as a compound of magnesium or calcium in the above-mentioned mixing process.

[0015] By the manufacture method of the positive active material concerning this invention which was mentioned above, since magnesium carbonate or calcium carbonate is used as a compound of magnesium or calcium, the positive active material obtained becomes the thing excellent in stability.

[0016] [ moreover, the manufacture method of the nonaqueous electrolyte cell of this invention ] When it is the manufacture method of the nonaqueous electrolyte cell equipped with the nonaqueous electrolyte which intervenes between a positive electrode, a negative electrode, and a positive electrode and a negative electrode and the above-mentioned positive electrode is produced, a cobalt compound, The compound of at least one sort of elements chosen from a lithium compound, an aluminium and chromium, vanadium, manganese, or iron, By calcinating the mixture obtained by the mixing process which mixes the compound of at least one sort of elements chosen from magnesium or calcium at a predetermined rate, and the above-mentioned mixing process General formula  $\text{LiCo}_x\text{A}_y\text{B}_z\text{O}_2$  (A expresses among a formula at least one sort chosen from aluminum, Cr, V, Mn, or Fe, and B expresses at least one sort chosen from Mg or Ca.) Moreover, x, y, and z are the number of the ranges of  $0.9\leq x<1$ ,  $0.001\leq y\leq 0.05$ , and  $0.001\leq z\leq 0.05$ , respectively. It has the baking process which obtains the compound expressed. And the manufacture method of the nonaqueous electrolyte cell of this invention is characterized by using magnesium carbonate or calcium carbonate as a compound of magnesium or calcium in the above-mentioned mixing process.

[0017] [ the manufacture method of the nonaqueous electrolyte cell concerning this invention which was mentioned above ] Since magnesium carbonate or calcium carbonate is used as a compound of magnesium or calcium when producing positive active material, the positive active material obtained becomes the thing excellent in stability, and the nonaqueous electrolyte cell excellent in the charge-and-discharge characteristics at the time of high temperature is obtained.

[0018]

[Mode for carrying out the invention] The form of operation of this invention is explained hereafter.

[0019] Drawing 1 is the longitudinal section showing the example of 1 composition of the nonaqueous electrolyte cell concerning this invention. As for this nonaqueous electrolyte cell 1, it comes to load [ the inside of a battery can 5 ] the rolled layer object around which the band-like positive electrode 2 and the band-like negative electrode 3 were wound in the state of adhesion through the separator 4.



[0020] The above-mentioned positive electrode 2 is produced by applying the positive electrode mixture containing positive active material and a binder on a collector, and drying. Metallic foils, such as aluminum foil, are used for a collector.

[0021] And with the nonaqueous electrolyte cell 1 of this invention, it is a general formula  $\text{LiCo}_x\text{AyBzO}_2$  (A expresses among a formula at least one sort chosen from aluminum, Cr, V, Mn, or Fe, and B expresses at least one sort chosen from Mg or Ca.) as positive active material. Moreover, x, y, and z are the number of the ranges of  $0.9 \leq x < 1$ ,  $0.001 \leq y \leq 0.05$ , and  $0.001 \leq z \leq 0.05$ , respectively. The lithium transition metal multiple oxide expressed is used.

[0022] The lithium Cobalt multiple oxide belongs to the hexagonal system expressed with R-3m of space groups, and has the crystal structure which a cobalt layer, an oxygen layer, and a lithium layer consist of by laminating in order. However, if charge progresses, lithium will be desorbed from a lithium layer, structure will destabilize, and a part of lamellar structure will collapse. If intercalation desorption of charge and discharge, i.e., lithium, is repeated, decay of structure will advance gradually and the reduction in capacity, i.e., cycle deterioration, will be caused. Under hot environments, since the thermal vibration of a constituent atom becomes intense, an above-mentioned decay process will be promoted and cycle deterioration will also be promoted more as a result.

[0023] Then, if a large aluminium, chromium, etc. of bond energy with oxygen replace a part of Cobalt, the structure of a charge state from which lithium escaped can become firm, and a cycle characteristic can be raised. However, into a crystal system, in order to make the atom with which descriptions differ exist, diffusion of the lithium ion within a crystal will be checked and capacity and charge-and-discharge efficiency fall.

[0024] Moreover, if magnesium and calcium from which valences differ replace lithium and Cobalt, it is known that electronic conduction nature will improve (for example, Solid Ionics 93 (1997) 227). However, if the amount of displacement by magnesium or calcium becomes large, it not only causes reduction in capacity, but it will promote decay of crystal structure.

[0025] Then, the 1st group which this invention persons become from an aluminium, chromium, vanadium, manganese, or iron about a lithium Cobalt multiple oxide, As a result of considering wholeheartedly the displacement in a small quantity by the 2nd group which consists of magnesium or calcium, when it used combining both groups, it found out that high-temperature characteristics excellent in high capacity were shown.

[0026] That is, by invention, it is a general formula  $\text{LiCo}_x\text{AyBzO}_2$  (A expresses among a formula at least one sort chosen from aluminum, Cr, V, Mn, or Fe, and B expresses at least one sort chosen from Mg or Ca.) about the chemical formula of positive active material. Moreover, x, y, and z are the number of the ranges of  $0.9 \leq x < 1$ ,  $0.001 \leq y \leq 0.05$ , and  $0.001 \leq z \leq 0.05$ , respectively. It specifies.

[0027] Here, in order that Cobalt which x contributes to charge and discharge in being smaller than 0.9 may decrease in number, capacity decreases. Moreover, when larger [ y ] than 0.05, as it mentioned above, diffusion of the lithium ion within a crystal will be checked, and capacity and charge-and-discharge efficiency will fall. In order to control this evil, as for y, 0.05 or less are desirable, and 0.03 or less are more preferably good. Moreover, since in z reduction in capacity and cycle deterioration advance as mentioned above also when larger than 0.05, as for z, 0.05 or less are desirable.

[0028] Stability of the lithium transition metal multiple oxide which has the presentation which was mentioned above improves not only at the time of ordinary temperature but at the time of high temperature. And the nonaqueous electrolyte cell 1 of this invention using such a lithium transition metal multiple oxide as positive active material becomes the thing excellent in the charge-and-discharge characteristics at the time of high temperature, and a cycle characteristic.

[0029] Moreover, as a binder of the above-mentioned positive electrode mixture, the well-known binder used for the positive electrode mixture of the cell can usually be used, and also well-known additives, such as an electric conduction agent, can be added to the above-mentioned positive electrode mixture.

[0030] A negative electrode 3 is produced by applying the negative electrode mixture containing the negative electrode active material and the binder of lithium in which dope and dedope are possible on a negative electrode collector, and drying. Although the metallic foil which does not make lithium and an alloy can be mentioned as a negative electrode collector, copper foil, nickel foil, etc. are especially desirable.

[0031] As negative electrode active material, polymer, such as a carbonaceous material and the charge of an alloy with large lithium capacity (quantity by which lithium may be doped), or polyacethylene, is used excluding lithium. As the above-mentioned carbonaceous material, carbon materials, such as a pyrolytic carbon [ in which dope and dedope of lithium are possible ], corks, graphite, vitrified carbon fiber, and organicity high molecular compound calcination object, carbon fiber, and activated carbon, can be used. The above-mentioned corks have a pitch coke, needle coke, a petroleum coke, etc. Moreover, the above-mentioned organic high molecular compound calcination object shows what calcinated and carbonized a phenol resin, furan resin, etc. at a suitable temperature.

[0032] Moreover, when lithium and a certain metallic element in which alloy formation is possible are set to M as the above-mentioned charge of an alloy, it is chemical formula  $MxM'yLiz$  (M' is one or more metallic elements other than Li element and M element.). Moreover, x is a larger numerical value than 0, and y and z are zero or more numerical values. It is the compound expressed. Suppose that elements which are furthermore semiconductor elements, such as B, Si, and As, are also included in a metallic element. If it illustrates, Mg, B,

aluminum, Ga, In, Si, Sn, Pb, They are Sb, Bi, Cd, Ag, Zn, Hf, Zr, each metals of Y and those alloy compounds, Li-aluminum, Li-aluminum-M (M consists or more of one of 2A, 3B, and 4B group transition metal elements.), AlSb, CuMgSb, etc.

[0033] as an element in which lithium and an alloy are possible, it is desirable to use 3B group typical element -- desirable -- Si or Sn -- it is Si still more preferably. If it illustrates, will be the compound expressed with  $M_xSi$  and  $M_xMn$  (one or more metallic elements excluding [ M ] Si or Sn respectively), and specifically They are  $SiB_4$ ,  $SiB_6$ ,  $Mg_2Si$ ,  $Mg_2Sn$ ,  $nickel_2Si$ ,  $TiSi_2$ ,  $MoSi_2$ ,  $CoSi_2$ ,  $NiSi_2$ ,  $CaSi_2$ ,  $CrSi_2$ ,  $Cu_5Si$ ,  $FeSi_2$ ,  $MnSi_2$ ,  $NbSi_2$ ,  $TaSi_2$ ,  $VSi_2$ ,  $WSi_2$ , and  $ZnSi_2$  grade.

[0034] Metallic elements other than 4B group except carbon containing one more or more nonmetallic elements may be contained. If it illustrates, they will be  $SiC$ ,  $Si_3N_4$ ,  $Si_2N_2O$ ,  $germanium_2N_2O$ ,  $S_1O_x$  ( $0 < x \leq 2$ ),  $SnO_x$  ( $0 < x \leq 2$ ),  $LiSiO$ ,  $LiSnO$ , etc.

[0035] To negative electrode active material, you may mix two or more sorts of material which was mentioned above. Dope of lithium to the above-mentioned material may be electrochemically performed within a cell after cell production, and even if cell production rear stirrups are supplied from sources of lithium other than a positive electrode or a positive electrode and are electrochemically doped before cell production, they are not cared about. Or it is compounded as a lithium content material in the case of material synthesis, and you may contain in the negative electrode at the time of cell production.

[0036] As a binder contained in a negative-electrode-active-material layer, a well-known resin material usually used as a binder of the negative-electrode-active-material layer of this kind of nonaqueous electrolyte cell can be used. Moreover, as a negative electrode 2, you may use for example, the metal lithium foil used as negative electrode active material.

[0037] A separator 4 can be allotted between a positive electrode 2 and a negative electrode 3, the short circuit by the physical contact with a positive electrode 2 and a negative electrode 3 can be prevented, and a well-known material usually used as a separator of this kind of nonaqueous electrolyte cell can be used, for example, high polymer films, such as polypropylene, are used. Moreover, the thickness of the relation between lithium ion conductivity and energy density to a separator needs a thing thin as much as possible. As for the thickness of a separator, specifically, 50 micrometers or less are desirable.

[0038] As nonaqueous electrolyte, the solution in which the aprotic nonaqueous solvent was made to dissolve an electrolyte is used.

[0039] As a nonaqueous solvent, for example Propylene carbonate, ethylene carbonate, Butylene carbonate, vinylene carbonate, gamma-butyl lactone, A sulfolane, a methyl sulfolane, 1, 2-dimethoxyethane, 1, 2-diethoxy ethane, Tetrahydrofuran, 2-methyl tetrahydrofuran, 1, 3-dioxolane, The 4-methyl 1, 3-dioxolane, methyl propionate, methyl butyrate, Dimethyl carbonate, diethyl carbonate, dipropyl carbonate, diethylether, acetonitrile, propionitrile,

anisole, acetate, butylate, propionate, etc. can be used. It is desirable to use catenoid carbonate, such as cyclic carbonate, such as propylene carbonate and vinylene carbonate, dimethyl carbonate, diethyl carbonate, and dipropyl carbonate, from a point of voltage stability especially. Moreover, one kind may be independently used for such a nonaqueous solvent, and two or more kinds may be mixed and it may be used for it.

[0040] Moreover, as an electrolyte dissolved in a nonaqueous solvent, the lithium salt of LiCl, LiBr, LiPF<sub>6</sub>, LiClO<sub>4</sub>, LiAsF<sub>6</sub>, LiBF<sub>4</sub>, LiCH<sub>3</sub>SO<sub>3</sub>, LiCF<sub>3</sub>SO<sub>3</sub>, LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>, and LiB(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub> grade can be used, for example. Also in these lithium salt, it is desirable to use LiPF<sub>6</sub> and LiBF<sub>4</sub>.

[0041] With the nonaqueous electrolyte cell 1 concerning this invention which was mentioned above, it is a general formula LiCoxAyBzO<sub>2</sub> (A expresses among a formula at least one sort chosen from aluminum, Cr, V, Mn, or Fe, and B expresses at least one sort chosen from Mg or Ca.) as positive active material. Moreover, x, y, and z are the number of the ranges of  $0.9 \leq x < 1$ ,  $0.001 \leq y \leq 0.05$ , and  $0.001 \leq z \leq 0.05$ , respectively. since the lithium transition metal multiple oxide expressed is used The stability of positive active material improves not only at the time of ordinary temperature but at the time of high temperature, and it becomes the thing excellent in the charge-and-discharge characteristics at the time of high temperature.

[0042] And the nonaqueous electrolyte cell 1 using such positive active material is produced as follows, for example.

[0043] First, the positive active material applied to this invention as follows is compounded.

[0044] The general formula LiCoxAyBzO<sub>2</sub> ([ A ] among a formula) concerning this invention Express at least one sort chosen from aluminum, Cr, V, Mn, or Fe, and [ B ] At least one sort chosen from Mg or Ca is expressed. [ the positive active material using the lithium transition metal multiple oxide expressed ] The compound of magnesium or calcium is further mixed with the compound of the element chosen from a cobalt compound, a lithium compound and an aluminium, chromium, vanadium, manganese, or iron at a predetermined rate, and it is obtained by calcinating this mixture. A burning temperature and firing time in particular are not limited.

[0045] It is made for x in a formula, y, and z to specifically become the number of the ranges of  $0.9 \leq x < 1$ ,  $0.001 \leq y \leq 0.05$ , and  $0.001 \leq z \leq 0.05$ , respectively.

[0046] As the above-mentioned cobalt compound, oxides and hydroxides, such as mineral salt of cobalt carbonate, a cobalt nitrate, etc. or cobalt oxide, can be used without restriction. It is possible to use mineral salt, an oxide, a hydroxide, etc. similarly about the compound of the element chosen from a lithium compound and an aluminium, chromium, vanadium, manganese, or iron.

[0047] Although it is possible to use mineral salt, an oxide, a hydroxide, etc. similarly about magnesium or a lime compound, in order to distribute and dissolve good in a crystal of

magnesium or a calcium atom, it is desirable to use mineral salt with low decomposition temperature. Therefore, as magnesium or calcium feed, since reactivity is high, it is effective to use carbonate, such as magnesium carbonate and calcium carbonate.

[0048] And a positive electrode 2 is produced by [ used as a positive electrode current collector ] applying and drying uniformly and forming a positive-active-material layer, for example on metallic foils, such as aluminum foil, in the positive electrode mixture containing the positive active material obtained as mentioned above and a binder. A well-known binder can be used as a binder of the above-mentioned positive electrode mixture, and also a well-known additive etc. can be added to the above-mentioned positive electrode mixture.

[0049] A negative electrode 3 is produced in the negative electrode mixture containing negative electrode active material and a binder by [ used as a negative electrode collector ] applying and drying uniformly and forming a negative-electrode-active-material layer, for example on metallic foils, such as copper foil. A well-known binder can be used as a binder of the above-mentioned negative electrode mixture, and also a well-known additive etc. can be added to the above-mentioned negative electrode mixture.

[0050] The positive electrode 2 obtained as mentioned above and a negative electrode 3 are stuck through the separator 4 which consists of a microporous polypropylene film, for example, and a rolled layer object is constituted by winding around a swirl type many times.

[0051] Next, an electric insulating plate 6 is intercalated in the bottom of the iron battery cans 5 which gave the nickel plate to the inside, and a rolled layer object is stored further. And in order to take current collection of a negative electrode, one end of the negative electrode lead 7 which consists of nickel, for example is made to stick to a negative electrode 3 by pressure, and the other end is welded to a battery can 5. Thereby, a battery can 5 will have a negative electrode 3 and a flow, and serves as an external negative electrode of the nonaqueous electrolyte cell 1. Moreover, in order to take current collection of a positive electrode 2, one end of the positive electrode lead 8 which consists of an aluminium, for example is attached to a positive electrode 2, and the other end is electrically connected with the cell lid 10 through the sheet metal 9 for electric current interception. This sheet metal 9 for electric current interception intercepts electric current according to cell internal pressure. Thereby, the cell lid 10 will have a positive electrode 2 and a flow, and serves as an external positive electrode of the nonaqueous electrolyte cell 1.

[0052] Next, nonaqueous electrolyte is poured in into this battery can 5. This nonaqueous electrolyte dissolves an electrolyte in a nonaqueous solvent, and is prepared.

[0053] By finally closing a battery can 5 through the insulating obturation gasket 11 which applied asphalt, the cell lid 10 is fixed and the cylindrical nonaqueous electrolyte cell 1 is produced.

[0054] In addition, as shown in drawing 1 in this nonaqueous electrolyte cell 1, while the center

pin 12 linked to the negative electrode lead 7 and the positive electrode lead 8 is formed When the pressure inside a cell becomes higher than a predetermined value, the PTC element 14 for preventing the rise in heat inside the safe valve gear 13 for extracting an internal gas and a cell is formed.

[0055] In addition, although the nonaqueous electrolyte cell 1 which used nonaqueous electrolyte as a nonaqueous electrolyte cell was mentioned as the example and the form of operation mentioned above explained it The composition of the nonaqueous electrolyte cell concerning this invention is not limited to composition which was mentioned above, but also when a solid electrolyte and the solid electrolyte with which matrix polymer comes to make nonaqueous electrolyte into the shape of a gel are used as nonaqueous electrolyte, it can be applied.

[0056] if it is the material which has lithium ion conductivity as a solid electrolyte -- an inorganic solid electrolyte and a solid polymer electrolyte -- all can be used. As an inorganic solid electrolyte, lithium nitride, lithium iodide, etc. are mentioned, for example. Moreover, a solid polymer electrolyte consists of electrolyte salt and a high molecular compound which distributes it, and as the high molecular compound concerned it is independent about ether system polymers, such as Pori (ethyleneoxide) and this bridge formation object, a Pori (methacrylate) ester system polymer, an acrylate system polymer, etc. -- or the inside of a molecule -- copolymerization -- or it can mix and use.

[0057] Various polymers can be used if nonaqueous electrolyte which was mentioned above is absorbed and gelled as matrix polymer used for a gel-like solid electrolyte. For example, ether system polymers, such as fluorine system polymers, such as Pori (vinylidene fluoride) and Pori (vinylidene fluoride co-hexafluoropropylene), and Pori (ethyleneoxide), this bridge formation object, or Pori (acrylonitrile) can be used. It is desirable to use a fluorine system polymer from oxidation reduction stability especially.

[0058] Moreover, although the secondary battery was mentioned as the example and the form of operation mentioned above explained it, this invention is not limited to this and can be applied also about a primary battery. Moreover, the cell of this invention is not limited in particular for the form, and can make cylindrical, a square shape, a coin type, a button type, a lamination seal type, etc. a thin shape and the various sizes of large-sized \*\*.

[0059]

[Working example] The example and comparative example which were hereafter performed in order to check the effect of this invention are explained. - Changing aluminum ratio for a part of Co, the nonaqueous electrolyte cell was produced using the lithium transition metal multiple oxide replaced with aluminum and Mg as positive active material, and the sample 1 shown in examination \*\*\*\* about the amount of aluminium displacement and the next - the sample 8 estimated those battery characteristics.

[0060] <Sample 1> It mixed so that it might be set to

Li:Co:aluminum:Mg=1.02:0.989:0.001:0.01 by a molar ratio, and commercial lithium carbonate, cobalt oxide, aluminium hydroxide, and magnesium carbonate were put into the crucible made from alumina, and were calcinated in desiccation atmosphere. When quantitative analysis of the obtained powder was carried out according to the atomic absorption method, the presentation of  $\text{LiCo}_{0.989}\text{aluminum}_{0.001}\text{Mg}_{0.01}\text{O}_2$  was checked. [ moreover, the pattern obtained when X diffraction measurement of this powder was performed ] It was similar to the pattern of  $\text{LiCoO}_2$  in 36-1004 of ICCD (International Centre For Diffraction Data), and forming the same lamellar structure as  $\text{LiCoO}_2$  was checked.

[0061] Polyvinylidene fluoride (PVdF) was mixed with 86 weight % for graphite as an electric conduction agent, 4 weight % was mixed with 10 weight % as a binder, N-methyl-2-pyrrolidone (NMP) was distributed, and positive active material produced as mentioned above was made into positive electrode mixture slurry. This slurry was uniformly compressed into both sides of 20-micrometer-thick band-like aluminum foil after spreading and desiccation and with a roller press machine, and the banding positive electrode was obtained. In addition, it was  $3.2\text{g/cm}^3$  when the pack density of this positive electrode was measured.

[0062] Next, PVdF was mixed 10weight % to 90 weight % of powdered artificial graphite as a negative electrode, NMP was distributed, and it was considered as negative electrode mixture slurry. This negative electrode mixture slurry was uniformly applied to both sides of 10-micron-thick copper foil, and the banding negative electrode was obtained by compressing with a roller press machine after desiccation.

[0063] Winding and a swirl type electrode object were produced for the banding positive electrode and banding negative electrode which were produced as mentioned above through the porous polyolefin film many times. This electrode object was stored to the iron battery cans which gave nickel plating, and the electric insulating plate has been arranged to up-and-down both sides of the electrode object concerned. Subsequently, the positive electrode lead made from an aluminium was drawn from the positive electrode current collector, and it welded to the projection part of the safety valve from which the cell lid and the electric flow were secured, and the negative electrode lead made from nickel was drawn from a negative electrode collector, and it welded to the bottom of the battery can.

[0064] On the other hand, the electrolyte dissolved  $\text{LiPF}_6$  and prepared nonaqueous electrolyte so that the volume mixing ratio of ethylene carbonate and methylethyl carbonate might become the concentration of  $1\text{ mol/dm}^3$  at the mixed solvent which is 1:1.

[0065] After pouring in an electrolyte finally into the battery can with which the above-mentioned electrode object was incorporated, by closing a battery can through an insulating obturation gasket, the safety valve, the PTC element, and the cell lid were fixed, and the outside diameter produced the 65-mm-high cylindrical nonaqueous electrolyte cell at 18mm.

[0066] <Sample 2> Lithium carbonate, cobalt oxide, and aluminium hydroxide,  $\text{LiCo}_{0.98}\text{aluminum}_{0.01}\text{Mg}_{0.01}\text{O}_2$  was compounded like the sample 1 except having mixed magnesium carbonate so that it might be set to  $\text{Li:Co:aluminum:Mg}=1.02:0.98:0.01:0.01$  by a molar ratio.

[0067] And the cylindrical nonaqueous electrolyte cell was produced like the sample 1, using this  $\text{LiCo}_{0.98}\text{aluminum}_{0.01}\text{Mg}_{0.01}\text{O}_2$  as positive active material.

[0068] <Sample 3> Lithium carbonate, cobalt oxide, and aluminium hydroxide,  $\text{LiCo}_{0.96}\text{aluminum}_{0.03}\text{Mg}_{0.01}\text{O}_2$  was compounded like the sample 1 except having mixed magnesium carbonate so that it might be set to  $\text{Li:Co:aluminum:Mg}=1.02:0.96:0.03:0.01$  by a molar ratio.

[0069] And the cylindrical nonaqueous electrolyte cell was produced like the sample 1, using this  $\text{LiCo}_{0.96}\text{aluminum}_{0.03}\text{Mg}_{0.01}\text{O}_2$  as positive active material.

[0070] <Sample 4> Lithium carbonate, cobalt oxide, and aluminium hydroxide,  $\text{LiCo}_{0.94}\text{aluminum}_{0.05}\text{Mg}_{0.01}\text{O}_2$  was compounded like the sample 1 except having mixed magnesium carbonate so that it might be set to  $\text{Li:Co:aluminum:Mg}=1.02:0.94:0.05:0.01$  by a molar ratio.

[0071] And the cylindrical nonaqueous electrolyte cell was produced like the sample 1, using this  $\text{LiCo}_{0.94}\text{aluminum}_{0.05}\text{Mg}_{0.01}\text{O}_2$  as positive active material.

[0072] <Sample 5> Lithium carbonate, cobalt oxide, and aluminium hydroxide,  $\text{LiCo}_{0.92}\text{aluminum}_{0.07}\text{Mg}_{0.01}\text{O}_2$  was compounded like the sample 1 except having mixed magnesium carbonate so that it might be set to  $\text{Li:Co:aluminum:Mg}=1.02:0.92:0.07:0.01$  by a molar ratio.

[0073] And the cylindrical nonaqueous electrolyte cell was produced like the sample 1, using this  $\text{LiCo}_{0.92}\text{aluminum}_{0.07}\text{Mg}_{0.01}\text{O}_2$  as positive active material.

[0074] <Sample 6> Lithium carbonate, cobalt oxide, and aluminium hydroxide,  $\text{LiCo}_{0.89}\text{aluminum}_{0.1}\text{Mg}_{0.01}\text{O}_2$  was compounded like the sample 1 except having mixed magnesium carbonate so that it might be set to  $\text{Li:Co:aluminum:Mg}=1.02:0.89:0.1:0.01$  by a molar ratio.

[0075] And the cylindrical nonaqueous electrolyte cell was produced like the sample 1, using this  $\text{LiCo}_{0.89}\text{aluminum}_{0.1}\text{Mg}_{0.01}\text{O}_2$  as positive active material.

[0076] <Sample 7>  $\text{LiCo}_{0.99}\text{Mg}_{0.01}\text{O}_2$  was compounded like the sample 1 except having mixed lithium carbonate, cobalt oxide, and magnesium carbonate not using aluminium hydroxide, so that it might be set to  $\text{Li:Co:Mg}=1.02:0.99:0.01$  by a molar ratio.

[0077] And the cylindrical nonaqueous electrolyte cell was produced like the sample 1, using this  $\text{LiCo}_{0.99}\text{Mg}_{0.01}\text{O}_2$  as positive active material.

[0078] <Sample 8>  $\text{LiCoO}_2$  was compounded like the sample 1 except having mixed lithium carbonate and cobalt oxide not using aluminium hydroxide and magnesium carbonate, so that



it might be set to Li:Co=1.02:1.0 by a molar ratio.

[0079] And the cylindrical nonaqueous electrolyte cell was produced like the sample 1, using this LiCoO<sub>2</sub> as positive active material.

[0080] [ cell / of the sample 1-8 produced as mentioned above / nonaqueous electrolyte ] After charging on the environmental temperature of 23 degrees C, the charge voltage 4.20V, the charging current of 1000mA, and the conditions of charge time 2.5 hours, it discharged with 1500mA of discharging current, and the final voltage 2.75V, and initial capacity (initial service capacity) was calculated. Moreover, initial efficiency was searched for as a ratio of the initial service capacity to initial charge capacity. Charge and discharge were repeated on the still more nearly same conditions, the service capacity of the 100 cycle eye was measured, and it asked for the capacity maintenance rate to initial capacity. Moreover, same measurement was performed under 60-degree C environment.

[0081] About the cell of a sample 1 - a sample 8, the 100 cycle capacity maintenance rate at initial capacity, initial efficiency, 23 degrees C, and 50 degrees C is combined with the ratio of aluminum and Mg, and is shown in Table 1.

[0082]

[Table 1]

	Al	Mg	初期容量 (mAh)	初期効率 (%)	23°C100サイクル 容量維持率(%)	50°C100サイクル 容量維持率(%)
サンプル1	0.001	0.010	1720	95.0	94.0	75.4
サンプル2	0.010	0.010	1700	95.0	95.3	81.8
サンプル3	0.030	0.010	1680	95.2	95.5	82.2
サンプル4	0.050	0.010	1690	94.9	94.4	82.0
サンプル5	0.070	0.010	1590	90.3	93.0	73.1
サンプル6	0.100	0.010	1470	85.5	92.2	64.9
サンプル7	0.000	0.010	1710	85.1	92.5	65.8
サンプル8	0.000	0.000	1710	95.0	93.2	72.1

[0083] With the sample 7 which replaced a part of Co only with Mg, even if compared with the Co unsubstituted sample 8, the capacity maintenance rate has fallen. On the other hand with the sample 1 which replaced a part of Co with aluminum and Mg - a sample 4, it turns out that the capacity maintenance rate is improving and the cycle characteristic in the time of ordinary temperature and high temperature is improved. However, in the case of the sample 5 and sample 6 with which the ratio of aluminum exceeds 0.05, early charge-and-discharge efficiency falls, and also the cycle characteristic has fallen. Therefore, the loadings y of aluminum was understood that it is desirable to consider it as the range of  $0.001 \leq y \leq 0.05$ .

[0084] - the examination about the amount of magnesium -- changing Mg ratio for a part of Co, the nonaqueous electrolyte cell was produced using the lithium transition metal multiple oxide replaced with aluminum and Mg as positive active material, and the sample 9 shown below - the sample 14 estimated those battery characteristics.

[0085] <Sample 9> Lithium carbonate, cobalt oxide, and aluminium hydroxide,

LiCo<sub>0.989</sub>aluminum<sub>0.01</sub>Mg<sub>0.001</sub>O<sub>2</sub> was compounded like the sample 1 except having mixed

magnesium carbonate so that it might be set to Li:Co:aluminum:Mg=1.02:0.989:0.01:0.001 by a molar ratio.

[0086] And the cylindrical nonaqueous electrolyte cell was produced like the sample 1, using this LiCo0.989aluminum0.01Mg 0.001O<sub>2</sub> as positive active material.

[0087] <Sample 10> Lithium carbonate, cobalt oxide, and aluminium hydroxide, LiCo0.96aluminum0.01Mg 0.03O<sub>2</sub> was compounded like the sample 1 except having mixed magnesium carbonate so that it might be set to Li:Co:aluminum:Mg=1.02:0.96:0.01:0.03 by a molar ratio.

[0088] And the cylindrical nonaqueous electrolyte cell was produced like the sample 1, using this LiCo0.96aluminum0.01Mg 0.03O<sub>2</sub> as positive active material.

[0089] <Sample 11> Lithium carbonate, cobalt oxide, and aluminium hydroxide, LiCo0.94aluminum0.01Mg 0.05O<sub>2</sub> was compounded like the sample 1 except having mixed magnesium carbonate so that it might be set to Li:Co:aluminum:Mg=1.02:0.94:0.01:0.05 by a molar ratio.

[0090] And the cylindrical nonaqueous electrolyte cell was produced like the sample 1, using this LiCo0.94aluminum0.01Mg 0.05O<sub>2</sub> as positive active material.

[0091] <Sample 12> Lithium carbonate, cobalt oxide, and aluminium hydroxide, LiCo0.92aluminum0.01Mg 0.07O<sub>2</sub> was compounded like the sample 1 except having mixed magnesium carbonate so that it might be set to Li:Co:aluminum:Mg=1.02:0.92:0.01:0.07 by a molar ratio.

[0092] And the cylindrical nonaqueous electrolyte cell was produced like the sample 1, using this LiCo0.92aluminum0.01Mg 0.07O<sub>2</sub> as positive active material.

[0093] <Sample 13> Lithium carbonate, cobalt oxide, and aluminium hydroxide, LiCo0.89aluminum0.01Mg 0.1O<sub>2</sub> was compounded like the sample 1 except having mixed magnesium carbonate so that it might be set to Li:Co:aluminum:Mg=1.02:0.89:0.01:0.1 by a molar ratio.

[0094] And the cylindrical nonaqueous electrolyte cell was produced like the sample 1, using this LiCo0.89aluminum0.01Mg 0.1O<sub>2</sub> as positive active material.

[0095] <Sample 14> Without using magnesium carbonate Lithium carbonate and cobalt oxide, LiCo0.99aluminum 0.01O<sub>2</sub> was compounded like the sample 1 except having mixed aluminium hydroxide so that it might be set to Li:Co:aluminum=1.02:0.99:0.1 by a molar ratio.

[0096] And the cylindrical nonaqueous electrolyte cell was produced like the sample 1, using this LiCo0.99aluminum 0.01O<sub>2</sub> as positive active material.

[0097] About the cell of a sample 9 - a sample 14, the 100 cycle capacity maintenance rate at the initial capacity measured as mentioned above, initial efficiency, 23 degrees C, and 50 degrees C is combined with the ratio of aluminum and Mg, and is shown in Table 2. In addition, Table 2 also shows both the evaluation results about the cell of a sample 2 and a

sample 8.

[0098]

[Table 2]

	A l	M g	初期容量 (mAh)	初期効率 (%)	23℃100% 容量維持率(%)	50℃100% 容量維持率(%)
サンプル9	0.010	0.001	1690	95.3	95.1	78.9
サンプル2	0.010	0.010	1700	95.0	95.3	81.8
サンプル10	0.010	0.030	1720	95.2	95.4	80.5
サンプル11	0.010	0.050	1710	95.1	94.4	77.2
サンプル12	0.010	0.070	1700	95.1	90.1	69.1
サンプル13	0.010	0.100	1710	94.9	84.3	63.3
サンプル14	0.010	0.000	1700	94.8	93.0	71.5
サンプル8	0.000	0.000	1710	95.0	93.2	72.1

[0099] With the sample 14 which replaced a part of Co only with aluminum, even if compared with the Co unsubstituted sample 8, the capacity maintenance rate has fallen. On the other hand with the sample 2 which replaced a part of Co with aluminum and Mg and a sample 9 - a sample 11, it turns out that the capacity maintenance rate is improving and the cycle characteristic in the time of ordinary temperature and high temperature is improved. However, in the case of the sample 12 and sample 13 with which the ratio of Mg exceeds 0.05, although the decline in early charge-and-discharge efficiency is not seen, the cycle characteristic has fallen. Therefore, the loadings  $z$  of Mg was understood that it is desirable to consider it as the range of  $0.001 \leq z \leq 0.05$ .

[0100] - the examination about the amount of chromium -- changing Cr ratio for a part of Co, the nonaqueous electrolyte cell was produced using the lithium transition metal multiple oxide replaced with Cr and Mg as positive active material, and the sample 15 shown below - the sample 20 estimated those battery characteristics.

[0101] <Sample 15> Replace with aluminium hydroxide and using chrome oxide Lithium carbonate,  $\text{LiCo}_{0.989}\text{Cr}_{0.001}\text{Mg}_{0.1}\text{O}_2$  was compounded like the sample 1 except having mixed cobalt oxide, chrome oxide, and magnesium carbonate so that it might be set to  $\text{Li}:\text{Co}:\text{Cr}:\text{Mg}=1.02:0.989:0.001:0.01$  by a molar ratio.

[0102] And the cylindrical nonaqueous electrolyte cell was produced like the sample 1, using this  $\text{LiCo}_{0.989}\text{Cr}_{0.001}\text{Mg}_{0.1}\text{O}_2$  as positive active material.

[0103] <Sample 16> Replace with aluminium hydroxide and using chrome oxide Lithium carbonate,  $\text{LiCo}_{0.98}\text{Cr}_{0.01}\text{Mg}_{0.01}\text{O}_2$  was compounded like the sample 1 except having mixed cobalt oxide, chrome oxide, and magnesium carbonate so that it might be set to  $\text{Li}:\text{Co}:\text{Cr}:\text{Mg}=1.02:0.98:0.01:0.01$  by a molar ratio.

[0104] And the cylindrical nonaqueous electrolyte cell was produced like the sample 1, using this  $\text{LiCo}_{0.98}\text{Cr}_{0.01}\text{Mg}_{0.01}\text{O}_2$  as positive active material.

[0105] <Sample 17> Replace with aluminium hydroxide and using chrome oxide Lithium carbonate,  $\text{LiCo}_{0.96}\text{Cr}_{0.03}\text{Mg}_{0.01}\text{O}_2$  was compounded like the sample 1 except having mixed cobalt oxide, chrome oxide, and magnesium carbonate so that it might be set to

Li:Co:Cr:Mg=1.02:0.96:0.03:0.01 by a molar ratio.

[0106] And the cylindrical nonaqueous electrolyte cell was produced like the sample 1, using this LiCo<sub>0.96</sub>Cr<sub>0.03</sub>Mg<sub>0.01</sub>O<sub>2</sub> as positive active material.

[0107] <Sample 18> Replace with aluminium hydroxide and using chrome oxide Lithium carbonate, LiCo<sub>0.94</sub>Cr<sub>0.05</sub>Mg<sub>0.01</sub>O<sub>2</sub> was compounded like the sample 1 except having mixed cobalt oxide, chrome oxide, and magnesium carbonate so that it might be set to Li:Co:Cr:Mg=1.02:0.94:0.05:0.01 by a molar ratio.

[0108] And the cylindrical nonaqueous electrolyte cell was produced like the sample 1, using this LiCo<sub>0.94</sub>Cr<sub>0.05</sub>Mg<sub>0.01</sub>O<sub>2</sub> as positive active material.

[0109] <Sample 19> Replace with aluminium hydroxide and using chrome oxide Lithium carbonate, LiCo<sub>0.92</sub>Cr<sub>0.07</sub>Mg<sub>0.01</sub>O<sub>2</sub> was compounded like the sample 1 except having mixed cobalt oxide, chrome oxide, and magnesium carbonate so that it might be set to Li:Co:Cr:Mg=1.02:0.92:0.07:0.01 by a molar ratio.

[0110] And the cylindrical nonaqueous electrolyte cell was produced like the sample 1, using this LiCo<sub>0.92</sub>Cr<sub>0.07</sub>Mg<sub>0.01</sub>O<sub>2</sub> as positive active material.

[0111] <Sample 20> Replace with aluminium hydroxide and using chrome oxide Lithium carbonate, LiCo<sub>0.89</sub>Cr<sub>0.1</sub>Mg<sub>0.01</sub>O<sub>2</sub> was compounded like the sample 1 except having mixed cobalt oxide, chrome oxide, and magnesium carbonate so that it might be set to Li:Co:Cr:Mg=1.02:0.89:0.1:0.01 by a molar ratio.

[0112] And the cylindrical nonaqueous electrolyte cell was produced like the sample 1, using this LiCo<sub>0.89</sub>Cr<sub>0.1</sub>Mg<sub>0.01</sub>O<sub>2</sub> as positive active material.

[0113] About the cell of a sample 15 - a sample 20, the 100 cycle capacity maintenance rate at the initial capacity measured as mentioned above, initial efficiency, 23 degrees C, and 50 degrees C is combined with the ratio of Cr and Mg, and is shown in Table 3. In addition, Table 3 also shows both the evaluation results about the cell of a sample 7 and a sample 8.

[0114]

[Table 3]

	Cr	Mg	初期容量 (mAh)	初期効率 (%)	23°C100回分 容量維持率(%)	50°C100回分 容量維持率(%)
サンプル7	0.000	0.010	1710	95.1	92.5	65.8
サンプル15	0.001	0.010	1710	95.1	93.8	75.5
サンプル16	0.010	0.010	1720	94.8	95.1	80.0
サンプル17	0.030	0.010	1670	94.6	95.0	81.1
サンプル18	0.050	0.010	1680	94.5	94.2	80.5
サンプル19	0.070	0.010	1580	88.1	92.3	70.2
サンプル20	0.100	0.010	1440	83.3	90.9	62.2
サンプル8	0.000	0.000	1710	95.0	93.2	72.1

[0115] With the sample 7 which replaced a part of Co only with Mg, even if compared with the Co unsubstituted sample 8, the capacity maintenance rate has fallen. On the other hand with the sample 15 which replaced a part of Co with Cr and Mg - a sample 18, it turns out that the capacity maintenance rate is improving and the cycle characteristic in the time of ordinary

temperature and high temperature is improved. However, in the case of the sample 19 and sample 20 with which the ratio of Cr exceeds 0.05, early charge-and-discharge efficiency falls greatly. Therefore, the loadings z of Cr was understood that it is desirable to consider it as the range of  $0.001 \leq z \leq 0.05$ .

[0116] - the examination about the amount of calcium -- changing Ca ratio for a part of Co, the nonaqueous electrolyte cell was produced using the lithium transition metal multiple oxide replaced by aluminum and Ca as positive active material, and the sample 21 shown below - the sample 26 estimated those battery characteristics.

[0117] <Sample 21> Replace with magnesium carbonate and using calcium carbonate Lithium carbonate,  $\text{LiCo}_{0.989}\text{aluminum}_{0.01}\text{Ca}_{0.001}\text{O}_2$  was compounded like the sample 1 except having mixed cobalt oxide, aluminium hydroxide, and calcium carbonate so that it might be set to  $\text{Li:Co:aluminum:Ca} = 1.02:0.989:0.01:0.001$  by a molar ratio.

[0118] And the cylindrical nonaqueous electrolyte cell was produced like the sample 1, using this  $\text{LiCo}_{0.989}\text{aluminum}_{0.01}\text{Ca}_{0.001}\text{O}_2$  as positive active material.

[0119] <Sample 22> Replace with magnesium carbonate and using calcium carbonate Lithium carbonate,  $\text{LiCo}_{0.98}\text{aluminum}_{0.01}\text{Ca}_{0.01}\text{O}_2$  was compounded like the sample 1 except having mixed cobalt oxide, aluminium hydroxide, and calcium carbonate so that it might be set to  $\text{Li:Co:aluminum:Ca} = 1.02:0.98:0.01:0.01$  by a molar ratio.

[0120] And the cylindrical nonaqueous electrolyte cell was produced like the sample 1, using this  $\text{LiCo}_{0.98}\text{aluminum}_{0.01}\text{Ca}_{0.01}\text{O}_2$  as positive active material.

[0121] <Sample 23> Replace with magnesium carbonate and using calcium carbonate Lithium carbonate,  $\text{LiCo}_{0.96}\text{aluminum}_{0.01}\text{Ca}_{0.03}\text{O}_2$  was compounded like the sample 1 except having mixed cobalt oxide, aluminium hydroxide, and calcium carbonate so that it might be set to  $\text{Li:Co:aluminum:Ca} = 1.02:0.96:0.01:0.03$  by a molar ratio.

[0122] And the cylindrical nonaqueous electrolyte cell was produced like the sample 1, using this  $\text{LiCo}_{0.96}\text{aluminum}_{0.01}\text{Ca}_{0.03}\text{O}_2$  as positive active material.

[0123] <Sample 24> Replace with magnesium carbonate and using calcium carbonate Lithium carbonate,  $\text{LiCo}_{0.94}\text{aluminum}_{0.01}\text{Ca}_{0.05}\text{O}_2$  was compounded like the sample 1 except having mixed cobalt oxide, aluminium hydroxide, and calcium carbonate so that it might be set to  $\text{Li:Co:aluminum:Ca} = 1.02:0.94:0.01:0.05$  by a molar ratio.

[0124] And the cylindrical nonaqueous electrolyte cell was produced like the sample 1, using this  $\text{LiCo}_{0.94}\text{aluminum}_{0.01}\text{Ca}_{0.05}\text{O}_2$  as positive active material.

[0125] <Sample 25> Replace with magnesium carbonate and using calcium carbonate Lithium carbonate,  $\text{LiCo}_{0.92}\text{aluminum}_{0.01}\text{Ca}_{0.07}\text{O}_2$  was compounded like the sample 1 except having mixed cobalt oxide, aluminium hydroxide, and calcium carbonate so that it might be set to  $\text{Li:Co:aluminum:Ca} = 1.02:0.92:0.01:0.07$  by a molar ratio.

[0126] And the cylindrical nonaqueous electrolyte cell was produced like the sample 1, using

this  $\text{LiCo}_0.92\text{aluminum}_{0.01}\text{Ca}_{0.07}\text{O}_2$  as positive active material.

[0127] <Sample 26> Replace with magnesium carbonate and using calcium carbonate Lithium carbonate,  $\text{LiCo}_0.89\text{aluminum}_{0.01}\text{Ca}_{0.1}\text{O}_2$  was compounded like the sample 1 except having mixed cobalt oxide, aluminium hydroxide, and calcium carbonate so that it might be set to  $\text{Li:Co:aluminum:Ca}=1.02:0.89:0.01:0.1$  by a molar ratio.

[0128] And the cylindrical nonaqueous electrolyte cell was produced like the sample 1, using this  $\text{LiCo}_0.89\text{aluminum}_{0.01}\text{Ca}_{0.1}\text{O}_2$  as positive active material.

[0129] About the cell of a sample 21 - a sample 26, the 100 cycle capacity maintenance rate at the initial capacity measured as mentioned above, initial efficiency, 23 degrees C, and 50 degrees C is combined with the ratio of Cr and Mg, and is shown in Table 4. In addition, Table 4 also shows both the evaluation results about the cell of a sample 8 and a sample 14.

[0130]

[Table 4]

	Al	Ca	初期容量 (mAh)	初期効率 (%)	23°C100回 容量維持率(%)	50°C100回 容量維持率(%)
サンプル14	0.010	0.000	1700	94.8	93.0	71.5
サンプル21	0.010	0.001	1710	95.1	95.2	78.5
サンプル22	0.010	0.010	1680	94.9	95.1	80.2
サンプル23	0.010	0.030	1690	94.8	95.5	81.1
サンプル24	0.010	0.050	1670	94.6	94.4	78.4
サンプル25	0.010	0.070	1660	94.5	89.3	67.8
サンプル26	0.010	0.100	1660	94.6	82.1	60.4
サンプル8	0.000	0.000	1710	95.0	93.2	72.1

[0131] With the sample 14 which replaced a part of Co only with aluminum, even if compared with the Co unsubstituted sample 8, the capacity maintenance rate has fallen. On the other hand with the sample 21 which replaced a part of Co by aluminum and Ca - a sample 24, it turns out that the capacity maintenance rate is improving and the cycle characteristic in the time of ordinary temperature and high temperature is improved. However, in the case of the sample 25 and sample 26 with which the ratio of Ca exceeds 0.05, although the decline in early charge-and-discharge efficiency is not seen, the cycle characteristic has fallen.

Therefore, the loadings  $z$  of Ca was understood that it is desirable to consider it as the range of  $0.001 \leq z \leq 0.05$ .

[0132] - the examination about various displacement elements -- the nonaqueous electrolyte cell was produced using the lithium transition metal multiple oxide which replaced a part of Co with aluminum, Cr, V, Mn, or Fe and Mg as positive active material, and the sample 27 shown below - the sample 29 estimated those battery characteristics.

[0133] <Sample 27> Replace with aluminium hydroxide and using vanadium oxide Lithium carbonate,  $\text{LiCo}_0.98\text{V}_{0.01}\text{Mg}_{0.01}\text{O}_2$  was compounded like the sample 1 except having mixed cobalt oxide, vanadium oxide, and magnesium carbonate so that it might be set to  $\text{Li:Co:V:Mg}=1.02:0.98:0.01:0.01$  by a molar ratio.

[0134] And the cylindrical nonaqueous electrolyte cell was produced like the sample 1, using

this  $\text{LiCo}_0.98\text{V}_0.01\text{Mg}_0.01\text{O}_2$  as positive active material.

[0135] <Sample 28> Replace with aluminium hydroxide and using manganese oxide Lithium carbonate,  $\text{LiCo}_0.98\text{Mn}_0.01\text{Mg}_0.01\text{O}_2$  was compounded like the sample 1 except having mixed cobalt oxide, manganese oxide, and magnesium carbonate so that it might be set to  $\text{Li}:\text{Co}:\text{Mn}:\text{Mg}=1.02:0.98:0.01:0.01$  by a molar ratio.

[0136] And the cylindrical nonaqueous electrolyte cell was produced like the sample 1, using this  $\text{LiCo}_0.98\text{Mn}_0.01\text{Mg}_0.01\text{O}_2$  as positive active material.

[0137] <Sample 29> Replace with aluminium hydroxide and using iron oxide Lithium carbonate,  $\text{LiCo}_0.98\text{Fe}_0.01\text{Mg}_0.01\text{O}_2$  was compounded like the sample 1 except having mixed cobalt oxide, iron oxide, and magnesium carbonate so that it might be set to  $\text{Li}:\text{Co}:\text{Cr}:\text{Mg}=1.02:0.98:0.01:0.01$  by a molar ratio.

[0138] And the cylindrical nonaqueous electrolyte cell was produced like the sample 1, using this  $\text{LiCo}_0.98\text{Fe}_0.01\text{Mg}_0.01\text{O}_2$  as positive active material.

[0139] About the cell of a sample 27 - a sample 29, the 100 cycle capacity maintenance rate at the initial capacity measured as mentioned above, initial efficiency, 23 degrees C, and 50 degrees C is combined with the ratio of aluminum, Cr, V, Mn, Fe, or Mg, and is shown in Table 5. In addition, Table 5 also shows both the evaluation results about the cell of a sample 2, a sample 16, and a sample 8.

[0140]

[Table 5]

	y	z	初期容量 (mAh)	初期効率 (%)	23°C100サイクル 容量維持率(%)	50°C100サイクル 容量維持率(%)
サンプル27	V:0.010	Mg:0.010	1680	94.9	95.0	78.8
サンプル28	Mn:0.010	Mg:0.010	1680	94.9	95.1	78.8
サンプル29	Fe:0.010	Mg:0.010	1690	94.8	94.8	78.7
サンプル2	Al:0.010	Mg:0.010	1700	95.0	95.3	81.8
サンプル16	Cr:0.010	Mg:0.010	1720	94.8	95.1	80.0
サンプル8	0.000	0.000	1710	95.0	93.2	72.1

[0141] [ a part of Co / the sample 2 replaced with aluminum, Cr, V, Mn or Fe, and Mg, a sample 16 and a sample 27 - a sample 29 ] so that clearly from Table 5 It turns out that the capacity maintenance rate is improving compared with the Co unsubstituted sample 8, and the cycle characteristic in the time of ordinary temperature and high temperature is improved. However, the effect of the cycle characteristic improvement at high temperature found that it was desirable to have appeared in the sample [ which used aluminum or Cr ] 2, and sample 16 case notably, and to use aluminum or Cr for it especially.

[0142] - the examination about the synthetic powder of positive active material -- the starting material was changed, positive active material was compounded, the nonaqueous electrolyte cell was produced using the positive active material, and the sample 30 shown below - the sample 31 estimated those battery characteristics.

[0143] <Sample 30>  $\text{LiCo}_0.98\text{aluminum}_0.01\text{Mg}_0.01\text{O}_2$  was compounded like the sample 1

except having replaced with magnesium carbonate and having used magnesium oxide.

[0144] And the cylindrical nonaqueous electrolyte cell was produced like the sample 1, using this  $\text{LiCo}_{0.98}\text{MnAl}_{0.01}\text{Mg}_{0.01}\text{O}_2$  as positive active material.

[0145] <Sample 31>  $\text{LiCo}_{0.98}\text{aluminum}_{0.01}\text{Ca}_{0.01}\text{O}_2$  was compounded like the sample 22 except having replaced with calcium carbonate and having used calcium oxide.

[0146] And the cylindrical nonaqueous electrolyte cell was produced like the sample 1, using this  $\text{LiCo}_{0.98}\text{MnAl}_{0.01}\text{Ca}_{0.01}\text{O}_2$  as positive active material.

[0147] About the cell of a sample 30 - a sample 31, the 100 cycle capacity maintenance rate at the initial capacity measured as mentioned above, initial efficiency, 23 degrees C, and 50 degrees C is combined with the synthetic powder of positive active material, and is shown in Table 6. In addition, Table 6 also shows both the evaluation results about the cell of a sample 2, a sample 22, and a sample 8.

[0148]

[Table 6]

	正極活物質 出発原料	初期容量 (mAh)	初期効率 (%)	23°C100サイクル 容量維持率(%)	50°C100サイクル 容量維持率(%)
サンプル30	酸化マグネシウム	1670	94.8	93.8	74.3
サンプル2	炭酸マグネシウム	1700	95.0	95.3	81.8
サンプル31	酸化カルシウム	1670	94.5	94.0	74.1
サンプル22	炭酸カルシウム	1680	94.9	95.1	80.2
サンプル8	—	1710	95.0	93.2	72.1

[0149] With the synthetic powder of positive active material especially the sample 30 using the oxide as a source of supply of Mg and Ca, and a sample 31, the effect of the cycle characteristic improvement has not fully shown up as compared with the sample 2 and sample 22 which used carbonate so that clearly from Table 6. Therefore, it turned out that it is desirable as the synthetic powder of positive active material, especially a source of supply of Mg and Ca to use carbonate.

[0150]

[Effect of the Invention] At this invention, it is a general formula  $\text{LiCo}_x\text{A}_y\text{B}_z\text{O}_2$  (A expresses among a formula at least one sort chosen from aluminum, Cr, V, Mn, or Fe, and B expresses at least one sort chosen from Mg or Ca.). Moreover, x, y, and z are the number of the ranges of  $0.9 \leq x < 1$ ,  $0.001 \leq y \leq 0.05$ , and  $0.001 \leq z \leq 0.05$ , respectively. It is using the lithium transition metal multiple oxide expressed as positive active material. The stability of the positive active material concerned can be raised not only at the time of ordinary temperature but at the time of high temperature, and the nonaqueous electrolyte cell excellent in the charge-and-discharge characteristics at the time of high temperature can be realized.

[Translation done.]